

Report for 2003ND27B: Modeling Groundwater Denitrification by Ferrous Iron Using PHREEQC

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Report Follows

MODELING GROUNDWATER DENITRIFICATION BY FERROUS IRON USING PHREEQC (Full Renewal)

PROBLEM DESCRIPTION

Nitrate is one of the most common groundwater contaminants (Gillham and Cherry, 1979, Fetter, 1994). Denitrification converts nitrate irreversibly into harmless nitrogen gas (Korom, 1992). It is a natural process that requires an anaerobic environment, denitrifying bacteria, and sufficient and reactive electron donating species (Korom, 1992; Starr and Gillham, 1993). Numerous researchers show that the availability of electron donors within aquifer sediments limits the denitrification potential of aquifers (Trudell et al., 1986; Robertson et al., 1996). Korom (1992) explained that the three common electron donors for denitrification are organic carbon, sulfide (usually as pyrite), and ferrous iron. Reduced manganese may also contribute to denitrification (Korom, 1992), but it has never been shown to be a significant electron donor for denitrification in an aquifer. Efforts by members of the UND denitrification research team show organic carbon and sulfide are active electron donors for denitrification in North Dakota and Minnesota. We also believe ferrous iron is an active electron donor; however, the geochemical evidence for ferrous iron is more difficult to demonstrate and requires comprehensive knowledge of the hydrogeochemistry of the research sites.

SCOPE AND OBJECTIVES

Denitrification in aquifers involves numerous hydrogeochemical processes with both the water and sediment phases. These include dilution, ion exchange, dissolution, precipitation, and oxidation-reduction reactions (Tesoriero et al., 2000). Knowledge of the above reactions will enable us to decipher the denitrification capacity of aquifers, particularly when ferrous iron minerals are involved. Therefore, our objective is to use PHREEQC in order to gain a more comprehensive understanding of the hydrogeochemical environment that governs denitrification by ferrous iron and associated aquifer reactions.

KEY LITERATURE AND PRIOR WORK

Figure 1 shows the nine sites in North Dakota and Minnesota currently being studied by the UND Denitrification Research Team.

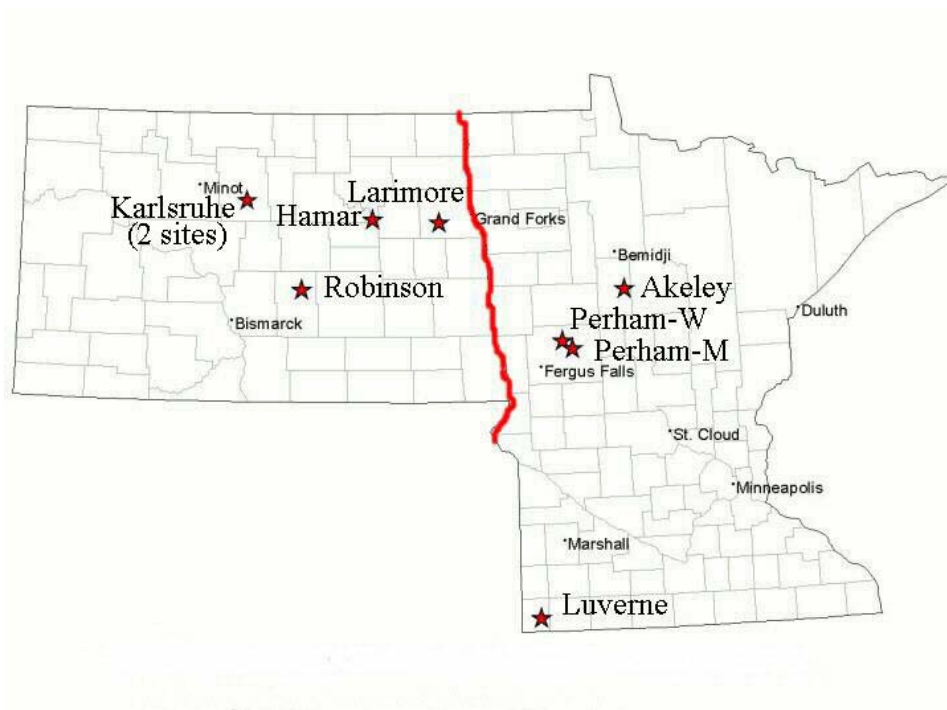


Figure 1. The nine in situ denitrification sites (indicated by stars) in Minnesota and North Dakota.

At each site stainless steel chambers partially isolate a portion of aquifer sediments, forming in situ mesocosms (ISMs). Tracer tests are performed in the ISMs and the resulting changes in the groundwater geochemistry in the chambers provides evidence for denitrification rates and what electron donors caused the denitrification. Schlag (1999) and Korom et al. (in review) describe how these sites are installed and how the tracer tests are performed. Results from the first tracer test done at the Larimore illustrate how an ISM tracer test is interpreted (Schlag, 1999; Korom et al., in review).

Figure 2 shows the trends of several major anions during the first tracer test at the Larimore site. Note that the nitrate concentrations decrease at a faster rate than the bromide concentrations. The latter decreases due to dilution with native groundwater during the tracer test. Only the nitrate lost beyond that explained by dilution of bromide is attributed to denitrification. Denitrification is commonly estimated by measuring the reaction products. The steep increase in sulfate indicates that sulfide was an electron donor for denitrification. Schlag (1999) and Korom et al. (in review) showed that about 60% of the denitrification can be explained by the oxidation of sulfide as pyrite.

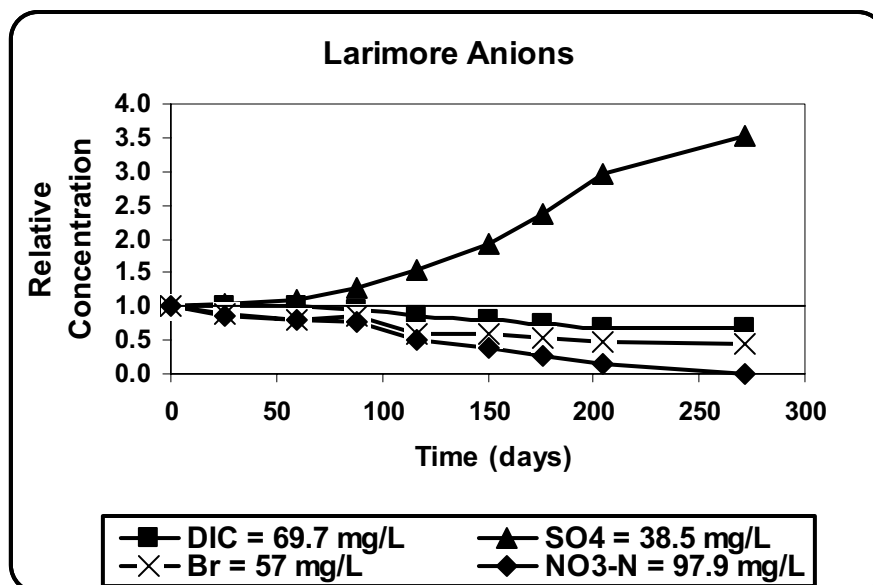


Figure 2. Anion concentrations during the first tracer test at the Larimore site. Initial concentrations are given in the box at the bottom of the figure.

Korom et al. (in review) also showed that organic carbon was likely responsible for most of the remaining denitrification observed. This process is illustrated by noting the decreasing dissolved inorganic carbon in Figure 2 and the steep loss of calcium and magnesium in Figure 3.

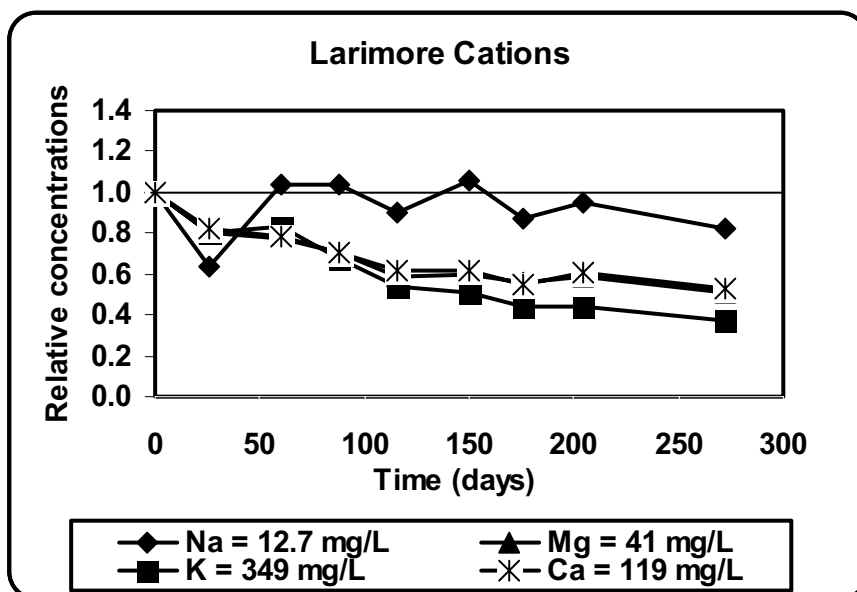


Figure 3. Cation concentrations during the first tracer test at the Larimore site. Initial concentrations are given in the box at the bottom of the figure.

Denitrification by organic carbon produces inorganic carbon. We expected DIC to increase in Figure 2. It would have, except the increase in inorganic carbon was masked by the precipitation of a magnesium-rich calcite (CaCO_3). Therefore, denitrification by sulfide results in an increase in sulfate; denitrification by organic carbon results in an increase in inorganic carbon, unless it is accompanied by a decrease in calcium (and possibly magnesium). In the latter case, the DIC will decrease, as well. (The decrease in potassium is mostly attributed to dilution because potassium bromide and potassium nitrate were added to the ISMs.)

We see these patterns in the groundwater in many of the ISMs. In fact the geochemical evidence in five of the research sites shows that organic carbon and inorganic sulfides play a major role in converting nitrates to nitrogen gas. However, both electron donors do not account for all the nitrate lost. Likewise, the reaction products of two sites, Robinson, ND and Akeley, MN, do not indicate the significant involvement of organic carbon or sulfides in the denitrification processes. Our hypothesis is that ferrous iron is the major electron donor causing reduction of nitrates in the latter two aquifers. (The tracer tests in the two ISMs near Minot just began this summer; it is too early to interpret the results).

Scope and Objectives

Mixing of nitrate polluted water and reduced waters at depth trigger important multiphase aquifer hydrogeochemical reactions. Some of the common aquifer geochemical reactions are ion exchange, dissolution and/or precipitation of dominant minerals, and redox reactions (Tesoriero et al., 2000). Knowledge of the above reactions, which is the main reason behind this proposal, enables us to decipher the denitrification capacity of aquifers. Therefore, our objective is to use PHREEQC in order to understand the hydrogeochemical environment that governs denitrification and other associated aquifer reactions, particularly with respect to the involvement of ferrous iron

Methods, Procedures and Facilities

Denitrification reactions require consideration of multiple thermodynamic and kinetic factors. Considering the net effects of these factors requires the application of realistic and relatively complex hydrogeochemical models. In this project PHREEQC (Parkhurst and Appelo, 1999) will be used to couple the regulating geochemical factors involved in the denitrification at the various ISM sites.

To study the controlling multiphase geochemical reactions both forward and inverse modeling schemes will be used. Forward modeling is constrained by equilibrium thermodynamics and the unknown variables are determined by solving the mass action equations. Inverse modeling is based on the net mass transfer among the interacting mineral phases in the initial and the final solutions. Mass balance modeling and cation exchange reactions are given special emphasis in the project. Since the results of inverse modeling are not unique, equilibrium and kinetic factors can be used to sort out improbable results.

Input files for the modeling are geochemical data of the native and injected waters as well as mineralogical data of the aquifers. Fortunately, substantial aqueous geochemical data including major anions, major cations, pH, and temperature, dissolved organic and inorganic carbon, of the study sites are available from previous work. Supplementary data required for the modeling are mineralogical composition, texture description, cation exchange capacity, organic carbon, inorganic sulfide and ferrous iron content of the sediments. Aquifer

sediment samples from the nine sites have been collected. Physical and geochemical analyses of the samples are ongoing and should be done by February, 2004. Analytical instruments in the UND Environmental Analytical Research Laboratory and the Department of Geology and Geological Engineering will be used for the water, sediment, and mineral analyses. Finally, modeling output will be compared with the field and laboratory results in order to verify both the numerical procedures as well as the hydrogeochemical reaction schemes.

ANTICIPATED RESULTS

The proposed analytical and modeling results are expected to provide insights into the denitrification capacity and electron donors involved at all the ISM sites. However, the particular focus herein is to provide further evidence whether ferrous iron is the major electron donor for denitrification at the Robinson, ND, and Akeley, MN, ISM sites.

PROGRESS TO DATE

Funding has been secured to repeat the tracer tests at the ND sites. In total, over half a million dollars in funding and in-kind matches has been provided thus far for this research. All data will be made available to me for this investigation. Preliminary interpretation of all the completed tracer tests has been done. Aquifer sediment samples of all the sites and much of the physical and geochemical analyses of the sediment samples are done. Of particular note are the preliminary results of the analyses of the iron coating the surface of the sediments shown below. The surface component is the most reactive fraction of the total ferrous iron in the sediments.

<u>Site</u>	<u>Ferrous Iron (%)</u>
Akeley	0.07
Hamar	0.006
Larimore	0.19
Perham2	0.02
Robinson	0.07

At the Hamar site, we observe little denitrification. However at the Perham2 site we have as much denitrification as at the Akeley and Robinson sites. Organic carbon appears to be the major electron donor for denitrification at the Perham2 site. We can not explain the denitrification at the Akeley and Robinson sites by either organic carbon or sulfide; our hypothesis is that ferrous iron is the electron donor. My preliminary analyses indicate that both of these sites have relatively high concentrations of reactive ferrous iron (3.5 times that of the Perham2 site), which supports our hypothesis. The Larimore site has even more ferrous iron, but it also has higher concentrations of organic carbon and sulfides, which may be used preferentially before the ferrous iron as an electron donor for denitrification.

In addition, PHREEQC has been shown to be effective in interpreting the denitrification reactions in the ISMs during the tracer tests (Skubinna, in preparation).

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